POLYCRYSTALLINE GROUP III METAL NITRIDE WITH GETTER AND METHOD OF MAKING

CROSS-REFERENCES TO RELATED APPLICATIONS

This application claims priority to Provisional Patent Application No. 61/122,332, filed Dec. 12, 2008, commonly assigned, and incorporated by reference herein for all purpose.

BACKGROUND OF THE INVENTION

The present invention generally relates to processing of materials for growth of crystals. More particularly, the present invention provides a crystalline nitride material suitable for use as a raw material for crystal growth of a gallium-containing nitride crystal by an ammonobasic or ammonoacidic technique, but there can be others. In other embodiments, the present invention provides methods suitable for synthesis of polycrystalline nitride materials, but it would be recognized that other crystals and materials can also be processed. Such crystals and materials include, but are not limited to, GaN, AlN, InN, InGaN, AlGaN, and AlInGaN, and others for manufacture of bulk or patterned substrates. Such bulk or patterned substrates can be used for a variety of applications including optoelectronic devices, lasers, light emitting diodes, solar cells, photoelectrochemical water splitting and hydrogen generation, photodetectors, integrated circuits, and transistors, among other devices.

Gallium nitride containing crystalline materials serve as substrates for manufacture of conventional optoelectronic devices, such as blue light emitting diodes and lasers. Such optoelectronic devices have been commonly manufactured on sapphire or silicon carbide substrates that differ in composition from the deposited nitride layers. In the conventional Metal-Organic Chemical Vapor Deposition (MOCVD) method, deposition of GaN is performed from ammonia and organometallic compounds in the gas phase. Although successful, conventional growth rates achieved make it difficult to provide a bulk layer of GaN material. Additionally, dislocation densities are also high and lead to poorer optoelectronic device performance.

Growth of nitride crystals by ammonothermal synthesis has been proposed. Ammonothermal crystal growth methods are expected to be scalable, as described by Dwilinski et al. [J. Crystal Growth 310, 3911 (2008)], by Ehrentraut, et al. [J. Crystal Growth 305, 204 (2007)], by D'Evelyn, et al. [J. Crystal Growth 300, 11 (2007)], and by Wang, et al. [Crystal Growth & Design 6, 1227 (2006)]. The ammonothermal method generally requires a polycrystalline nitride raw material, which is then recrystallized onto seed crystals. An ongoing challenge of ammonothermally-grown GaN crystals is a significant level of impurities, which cause the crystals to be colored, e.g., yellowish, greenish, grayish, or brownish. The residual impurities may cause optical absorption in light emitting diodes fabricated on such substrates, negatively impacting efficiency, and may also degrade the electrical conductivity and/or generate stresses within the crystals. One source of the impurities is the polycrystalline nitride raw material.

For example, gallium nitride crystals grown by hydride vapor phase epitaxy, a relatively more expensive, vapor phase method, have demonstrated very good optical transparency, with an optical absorption coefficient below 2 cm^{-1} at wavelengths between about 385 nanometers and about 620 nanometers [Oshima, et al., J. Appl. Phys. 98, 103509 (2005)]. However, the most transparent ammonothermally-grown gallium nitride crystals of which we are aware were yellowish and had an optical absorption coefficient below 5 cm^{-1} over the wavelength range between about 465 nanometers and about 700 nanometers [D'Evelyn, et al., J. Crystal Growth 300, 11 (2007) and U.S. Pat. No. 7,078,731].

Several methods for synthesis of polycrystalline nitride materials have been proposed. Callahan, et al. [MRS Internet J. Nitride Semicond. Res. 4, 10 (1999); U.S. Pat. No. 6,406,540] proposed a chemical vapor reaction process involving heating gallium metal in a vapor formed by heating NH_4Cl. Related methods have been discussed by Wang, et al. [J. Crystal Growth 286, 50 (2006)] and by Park, et al. [U.S. Patent applications 2007/0142204, 2007/0151509 and 2007/0141819], all of which are hereby incorporated by reference in their entirety. The predominant impurity observed was oxygen, at levels varying from about 16 to about 160 parts per million (ppm). The chemical form of the oxygen was not specified. An alternative method, involving heating in ammonia only and producing GaN powder with an oxygen content below 0.07 wt %, was disclosed by Tsuji [U.S. Patent application 2008/0193363], which is hereby incorporated by reference in its entirety. Yet another alternative method, involving contacting Ga metal with a wetting agent such as Bi and heating in ammonia only, producing GaN powder with an oxygen content below 650 ppm, has been disclosed by Spencer, et al. [U.S. Pat. No. 7,381,391], which is hereby incorporated by reference in its entirety.

What is needed is a method for low-cost manufacturing of polycrystalline nitride materials that are suitable for crystal growth of bulk gallium nitride crystals and do not contribute to impurities in the bulk crystals.

BRIEF SUMMARY OF THE INVENTION

According to the present invention, techniques related to processing of materials for growth of crystals are provided. More particularly, the present invention provides a crystalline nitride material suitable for use as a raw material for crystal growth of a gallium-containing nitride crystal by an ammonobasic or ammonoacidic technique, but there can be others. In other embodiments, the present invention provides methods suitable for synthesis of polycrystalline nitride materials, but it would be recognized that other crystals and materials can also be processed. Such crystals and materials include, but are not limited to, GaN, AlN, InN, InGaN, AlGaN, and AlInGaN, and others for manufacture of bulk or patterned substrates. Such bulk or patterned substrates can be used for a variety of applications including optoelectronic devices, lasers, light emitting diodes, solar cells, photoelectrochemical water splitting and hydrogen generation, photodetectors, integrated circuits, and transistors, among other devices.

In a specific embodiment, the present invention provides a composition for a material. The composition includes a polycrystalline group III metal nitride material having a plurality of grains. Preferably, the plurality of grains are characterized by a columnar structure. In a specific embodiment, one or more of the grains have an average grain size in a range of from about 10 nanometers to about 1 millimeter. The composition has an atomic fraction of a group III metal in the group III metal nitride in a range of from about 0.49 to about 0.55. In one or more embodiments, the metal in the group III metal nitride is selected from at least aluminum, indium, or gallium. The composition also has an oxygen content in the group III metal nitride material provided as a group III metal oxide or